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DIVISION S-8—NUTRIENT MANAGEMENT & SOIL & PLANT ANALYSIS

Predicting Phosphorus Desorption from Mid-Atlantic Coastal Plain Soils

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ABSTRACT

Pollution of surface waters by P from agricultural areas is a water quality issue in Delaware. The FHANTM 2.0 computer model can help identify areas with a high potential for P loss, but the model's representation of P desorption from soils to runoff waters needs re-evaluation. The equation, $P_d = K P_o t^\alpha W^\beta$, has been proposed to predict such P desorption, but equations originally proposed to predict values for the constants K , α , and β from the ratio of soil clay content/soil organic C content may not be accurate for Delaware soils. Therefore, we measured P desorption for 23 sandy Delaware soils for times of 5 to 180 min, water/soil ratios of 10 to 1000 L kg⁻¹, and three initial levels of soil desorbable P. Values for the constants K , α , and β were calculated and related to soil properties. We found that K , α , and β values were not well related to clay/OC, but were better related to the ratio of oxalate-extractable Fe/OC content (α) or the sum of oxalate extractable Fe and Al (β and K). These results can be used to help refine the FHANTM 2.0 model in predicting P loss from agricultural areas in Delaware and similar landscapes in the Mid-Atlantic Coastal Plain.

THE NONPOINT SOURCE POLLUTION of surface waters by P is an international environmental quality issue. In Delaware, water quality in the Inland Bays national estuary, which consists of the Rehoboth, Indian River, and Little Assawoman Bays, has been impaired by P to such an extent that the state must now comply with regulations of the Clean Water Act (United States, 1967). As part of this compliance, total maximum daily loads (TMDL) have been established as the level of pollution below which the Inland Bays will meet water quality standards. One goal of the TMDLs is a 70% reduction of nonpoint source P loads to the Inland Bays (State of Delaware, 1995). Because agriculture has been identified as a significant nonpoint source of P in the Inland Bays watershed (Ritter, 1992), it is necessary to identify agricultural areas that have a high potential for P export.

Field-scale nutrient transport models have been proposed as a means to characterize the environmental risk

of agricultural P to water quality. In Florida, FHANTM 2.0 (Field Hydrologic and Nutrient Transport Model, version 2.0; Fraisse and Campbell, 1997) was developed to simulate water and P movement from individual fields as part of an effort to reduce P loads to Lake Okeechobee. The hydrology of FHANTM 2.0 is based on DRAINMOD (Skaggs, 1980), and the nutrient components are based on GLEAMS (Leonard, 1987). Because Florida's physical and hydrologic conditions of flat fields, high water tables, and high P sandy soils are similar to those in Delaware, FHANTM 2.0 could potentially be used in Delaware to simulate field-scale P export. However, several of FHANTM 2.0's mathematical representations of soil P processes were designed either for pesticide transformations in soils for GLEAMS or for specific chemical and physical properties of Florida soils. Therefore, to use FHANTM 2.0 in Delaware, its P components must be modified to more accurately represent the chemical and physical processes in Delaware soils. One such modification is the representation of P desorption to runoff waters. Currently in FHANTM 2.0, the quantity of P in the topsoil available for runoff, $(C_{av})_p$ (mg kg⁻¹), is calculated with the equation

$$(C_{av})_p = (CPLAB) \exp \{[-(Pr - Q - AWS)] / [(SSG) K_d (1 - POR) + POR]\}, \quad [1]$$

Abbreviations: Al_{ox}, acid ammonium oxalate-extractable Al; AWS, amount of rainfall needed to saturate the topsoil layer in the FHANTM 2.0 model; B , extraction coefficient used in the FHANTM 2.0 model; $(C_{av})_p$, quantity of P in the topsoil available for runoff used in the FHANTM 2.0 model; CPLAB, quantity of desorbable P in the topsoil used in the FHANTM 2.0 model; $(C_w)_p$, concentration of P in runoff used in the FHANTM 2.0 model; Fe_{ox}, acid ammonium oxalate-extractable Fe; FHANTM, Field Hydrologic and Nutrient Transport Model; OC, organic C; OM, organic matter; UDSTP, University of Delaware Soil Testing Program; K , empirical constant in soil P desorption equation; K_d , partitioning coefficient used in the FHANTM 2.0 model; P_d , amount of P desorbed from the soil; P_o , initial concentration of desorbable P in soil; POR, porosity used in the FHANTM 2.0 model; Pr, value for precipitation used in the FHANTM 2.0 model; Q , value for runoff used in the FHANTM 2.0 model; SSG, soil specific gravity used in the FHANTM 2.0 model; t , time of P desorption; TMDL, total maximum daily load; W , water/soil ratio during P desorption; α , empirical constant in soil P desorption equation; β , empirical constant in soil P desorption equation.

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where CPLAB (mg kg^{-1}) is the quantity of labile P in the topsoil as defined for the FHANTM 2.0 model, Pr (cm) is precipitation, Q (cm) is runoff, AWS (cm) is the amount of rainfall necessary to fill the topsoil layer to saturation, SSG (g cm^{-3}) is soil specific gravity, K_d is a partitioning coefficient, and POR is soil porosity (cm cm^{-1}). Given that the values of SSG , K_d , and POR are constant for a given soil and that the value of AWS is much less than Pr and Q , Eq. [1] mathematically demonstrates that $(C_{av})_p$ is curvilinearly related to CPLAB as a function of the absolute value of the difference between Pr and Q . Essentially, as the difference between Pr and Q decreases, the amount of P available for runoff increases. The actual concentration of P in runoff, $(C_w)_p$ (mg L^{-1}), is then calculated in FHANTM 2.0 based on partitioning (K_d) and extraction (B) coefficients with the Eq. [2].

$$(C_w)_p = [(C_{av})_p B] / [1 + (K_d) B] \quad [2]$$

The partitioning coefficient, K_d , assumes that the equilibrium relationship between $(C_{av})_p$ and $(C_w)_p$ is linear and is a function of the Mg and OC content of the topsoil. The extraction coefficient, B , accounts for the fact that the concentration of P in runoff is typically less than the P concentration in the soil solution and is calculated based on the value of the soil's K_d value. Because Eq. [1] and [2] were originally designed to represent pesticide transformations in soils (Leonard et al., 1987), and were calibrated in FHANTM 2.0 for Florida soils, they may not accurately represent desorption of P from soils to runoff for conditions in Delaware.

In many studies of P desorption, it is commonly observed that desorption reactions occur rapidly at first and then decrease as equilibrium is approached. It is also observed that the quantity of P desorbed is largely a function of the time allowed for desorption and the water/soil ratio during desorption (Barrow, 1979). Such desorption data are typically best described by exponential or logarithmic equations, such as Elovich or Freundlich equations (Chien and Clayton, 1980; Kuo and Lotse, 1974). Sharpley et al. (1981) proposed a simplified P desorption equation:

$$P_d = KP_0 t^\alpha W^\beta \quad [3]$$

where P_d is the amount of P desorbed (mg kg^{-1}) in time, t (min), at a water/soil ratio W (mL g^{-1}), P_0 is the initial amount of desorbable P present in the soil (mg kg^{-1}), and K , α , and β are empirical constants for a given soil. Equation [3] represents a significant improvement from the current P desorption equations in FHANTM 2.0 (Eq. [1] and [2]) because it accounts for the nonlinear characteristics of P desorption and the strong influence of time and water/soil ratio. For any given runoff event, either simulated or observed, the time, water/soil ratio, and desorbable P parameters are either known, as is the case with FHANTM 2.0, or can be easily measured or calculated. Sharpley (1983) pointed out that the application of Eq. [3] is limited if the values of the constants K , α , and β must be experimentally determined for a given soil before P desorption can be predicted. Application of Eq. [3] is much broader if the values for the

constants can be predicted from known or easily estimated soil physical and chemical properties. Therefore, Sharpley (1983) related K , α , and β to soil properties and found statistically significant relationships with the ratio of soil Fe/OC and clay to OC for 43 soils collected from throughout the USA. However, the clay and Fe contents of these soils were much greater than those typically found in the sandy soils of Delaware's Inland Bays watershed and of the Mid-Atlantic Coastal Plain in general. Because the clay and Fe contents of soils have a strong influence on P desorption phenomena, the relationships provided by Sharpley to predict K , α , and β and to subsequently predict P desorption may not accurately represent Delaware soils. Given these considerations, the objectives of this research were to determine if Sharpley's relationships for predicting K , α , and β are applicable to Delaware soils; and, if not, to develop relationships for predicting K , α , and β from known or easily measured properties of Delaware soils. Although the research presented here was conducted for only Delaware soils, it should be applicable to Mid-Atlantic Coastal Plain soils with similar physical and chemical characteristics.

MATERIALS AND METHODS

Soil Selection and Characterization

Twenty soil samples were obtained from the archives of the University of Delaware Soil Testing Program (UDSTP). These soil samples had been used in a previous study to assess relationships between soil test P, soluble P, and P saturation (Pautler and Sims, 2000). Of Delaware's three counties, two soil samples were taken from the northernmost New Castle County, 12 were taken from the southernmost Sussex County, and six were taken from Kent County. An additional three soil samples were taken from samples collected from a Sussex County field site that was used in a previous study to assess the impact of agricultural drainage on water quality (Sims et al., 1998). These three soil samples were chosen because they represent the artificially drained, high organic matter (OM) soils that will likely be subject to future simulations of P export using the modified FHANTM 2.0 model. The number of soil samples from each county was chosen to reflect the percentage of samples submitted to the UDSTP each year. Overall, the 23 soil samples were chosen to represent a range in clay, Fe and Al oxide, and OM content, all of which have a strong influence on P desorption. The quantity of desorbable P initially present in the soil samples was a secondary consideration.

All samples had been previously air-dried and ground to pass a 2.0-mm sieve. We characterized the soils for pH (1:1 soil/water ratio), soil test P (STP; Mehlich-1 extraction; 1:4 ratio of soil/0.05 M HCl + 0.0125 M H_2SO_4 ; 5-min reaction time [Sims and Heckendorn, 1991]), particle size by the hydrometer method (Bouyoucos, 1962), and acid ammonium oxalate-extractable Al and Fe (Al_{ox} and Fe_{ox} ; 1:40 ratio of soil/0.2 M $[\text{NH}_4]_2\text{C}_2\text{O}_4$; 2-h reaction time in darkness [McKeague and Day, 1996]). Soil OC was measured by the Walkley-Black wet oxidation procedure (Nelson and Sommers, 1982). The initial amount of desorbable P (P_0 , Eq. [3]) was measured with Fe-oxide impregnated filter strips (1:40 ratio of soil/0.01 M CaCl_2 + Fe-oxide coated filter paper strip; 16-h reaction time, followed by desorption of P with 1 M H_2SO_4 [Chardon et al., 1996]). The P in the Mehlich-1 extraction and the Fe and Al in the

oxalate extraction were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The P in the filter strip procedure was measured by the molybdate blue method of Murphy and Riley (1962) with absorbance measured at 882 nm.

Phosphorus Desorption Experiments

The desorbable P status of each soil was varied by adding 0, 95, and 190 mg P kg⁻¹ soil as a solution of KH₂PO₄ (equivalent to fertilizer application rates of 0, 50, and 100 kg P ha⁻¹ to a 4-cm soil depth). Both the P-amended and unamended soils were incubated at 25°C for 3 d prior to the P desorption study. This incubation time was chosen to duplicate the experiments of Sharpley et al. (1981), and because Sharpley and Ahuja (1982) showed that longer incubation times did not have a significant effect on the values of K , α , and β . The desorption of P from soils was investigated by shaking duplicate samples with distilled water at water/soil ratios of 10:1, 100:1, and 1000:1 (mL g⁻¹) on an end-to-end shaker at 25°C for times of 5, 30, 60, and 180 min. After shaking, each solution was filtered through Gelman 0.45- μ m millipore filters (Gelman Sciences, Ann Arbor, MI). The P in the filtered solutions was measured colorimetrically on a Sequoia-Turner model 340 spectrophotometer (Sequoia Turner Corp., Mountain View, CA) by the molybdate blue method of Murphy and Riley (1962) with absorbance measured at 882 nm.

Calculation of K , α , and β

Given that Eq. [3] is valid and is a power equation, at any given combination of W and P_o , the logarithm of P_d should be linearly related to the logarithm of t for each soil. The slope of this line is the value of α for that soil at that combination of W and P_o . Similarly, at any given combination of t and P_o , the logarithm of P_d should be linearly related to the logarithm of W for each soil. The slope of this line is the value of β for that soil at that combination of t and P_o . In the final case, at any given combination of t and W , P_d should be linearly related to P_o . The slope of this line is the value of K for that soil at that combination of t and W . Throughout the desorption experiments for each soil, nine values of α from all combinations of W and P_o , 12 values of β from all combinations of t and P_o , and 12 values of K from all combinations of t and W were calculated. Average values of α , β , and K were then calculated from these nine or 12 values. These average values of α , β , and K were then related to soil properties using a least-squares regression. The parameters of the resulting regression equations and their correlation coefficients were analyzed for significance by an ANOVA procedure. These statistical analyses were performed within Microsoft EXCEL spreadsheets (Microsoft, Inc., Redmond, WA). Correlation coefficients of the regression equations were compared for statistically significant differences as described by Snedecor and Cochran

(1971). To do this, r values were converted to z values using statistical tables. The differences between z values were then tested for significance using a two-tailed t test. These comparisons were made only among equations for each constant α , β , and K , and not between constants.

RESULTS AND DISCUSSION

Soil Characteristics

The soils used in this study were representative of many soils in the Coastal Plain and Piedmont regions of Delaware and other Mid-Atlantic states. In general, soils were moderately acidic and low in OC, although this varied slightly among counties (Table 1). Soils from New Castle County, which is in the Piedmont plateau, are generally finer-textured (silt loams) than the Coastal Plain soils from Kent and Sussex Counties (sandy loams and loamy sands). The dominant soil orders in New Castle and Kent Counties are Ultisols (80–90%) and Alfisols (9%). The soils of Sussex County are typically very sandy with low OC, although some may have high OC because of poor drainage. Dominant soil orders in Sussex County are Ultisols (57%) and Entisols (33%).

The average OC content of the 23 Delaware soils (1277 mmol kg⁻¹) was comparable with the average OC content of Sharpley's (1983) 43 soils (1083 mmol kg⁻¹), but the Delaware soils on average had less clay (86 g kg⁻¹) than Sharpley's soils (220 g kg⁻¹). The average Fe_{ox} and Al_{ox} contents of the Delaware soils (Fe_{ox} = 8 mmol kg⁻¹ and Al_{ox} = 32 mmol kg⁻¹) were also much less than the extractable Fe and Al contents of Sharpley's soils (Fe = 98 mmol kg⁻¹ and Al = 208 mmol kg⁻¹). Sharpley used 1 M NH₄Oac, pH 4.8, to extract Fe and Al, whereas we used 0.2 M (NH₄)₂C₂O₄. Therefore, some of the difference in the amount of Fe and Al content extracted from Sharpley's and our Delaware soils is likely because of the difference in the inherent ability of acetate and oxalate to extract Fe and Al from soil. However, the literature is sparse with research directly comparing the ability of acetate and oxalate to extract soil Fe and Al. Myers et al. (1988) extracted Al from seven acid Ohio soils with both 1 M NH₄Oac, pH 4.8, and 0.2 M (NH₄)₂C₂O₄ and found that the oxalate always extracted more Al than the acetate, by an average greater amount of nearly nine times. The same is likely true for soil Fe, but we could not find any sources in the literature that directly compare the ability of oxalate and acetate to extract Fe from soil. Indirectly, Kraske et al. (1989) extracted Fe from six New England

Table 1. Selected soil physical and chemical properties of 23 Delaware soils used for P desorption studies.

Property	All soils	New Castle soils	Kent soils	Sussex soils
		Mean \pm SD†		
Sand, g kg ⁻¹	688 \pm 147	417 \pm 188	704 \pm 93	740 \pm 88
Clay, g kg ⁻¹	86 \pm 44	148 \pm 76	74 \pm 29	78 \pm 33
pH	6.0 \pm 0.7	6.4 \pm 0.1	6.2 \pm 0.3	5.8 \pm 0.8
OC, mmol kg ⁻¹	1277 \pm 1432	778 \pm 148	789 \pm 279	1593 \pm 1778
Al _{ox} , mmol kg ⁻¹	32 \pm 24	27 \pm 13	24 \pm 7	37 \pm 29
Fe _{ox} , mmol kg ⁻¹	8 \pm 4	11 \pm 2	8 \pm 2	8 \pm 5
Mehlich-1 P, mg kg ⁻¹	87 \pm 82	32 \pm 13	144 \pm 130	74 \pm 49
Desorbable P, mg kg ⁻¹ ‡	32 \pm 19	17 \pm 11	40 \pm 26	31 \pm 17

† Mean \pm Standard Deviation.

‡ P measured with Fe-oxide impregnated filter strips in unamended soils.

forest soils with both 1 M NH_4Oac , pH 4.8, and Mehlich 3 (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.01 M HNO_3 + 0.001 M EDTA) and found that the Mehlich 3 always extracted more Fe than the acetate, by an average greater amount of 22 times. Comparatively, research from the University of Delaware (J.T. Sims, unpublished data, 2000) that extracted Fe from 96 Delaware soil samples with both oxalate and Mehlich 3 shows that oxalate always extracted more Fe than Mehlich 3, by an average greater amount of six times. Therefore, if oxalate extracts more Fe from soils than Mehlich 3, and Mehlich 3 extracts more Fe from soils than acetate, then oxalate extracts more Fe from soils than acetate. All this research provides evidence that Sharpley extracted more Fe and Al with acetate from his soils than we extracted with oxalate from our Delaware soils because his soils actually contained more Fe and Al and not because acetate is generally capable of extracting more Fe and Al from soils than oxalate. The point of the above discussion is to show that the properties of Sharpley's soils that he used to predict K , α , and β values, specifically clay and Fe content, were significantly different from those in our Delaware soils. This is a key consideration in regard to the objectives of our research. Because Sharpley's soils contained much more clay and Fe than our soils, we hypothesized that the relationships he developed between soil clay or Fe content and values for K , α , β would not be accurate for Delaware soils.

Phosphorus Desorption Characteristics

The term P_0 in Eq. [3] represents the amount of soil P that can potentially be desorbed to water for the time periods and water/soil ratios used during our experiments. Sharpley and Ahuja (1982) stated that P_0 represents the amount of soil P that is potentially readily desorbable with water, especially under conditions that would occur during a runoff event. The cutoff point between readily desorbable P and more slowly desorbable P is based on where the kinetic mechanism of desorption shows a change from one to the other. The cutoff point may be somewhat arbitrary, but the applicability of Eq. [3] is not affected as long as the method to estimate P_0 is consistently used. In Sharpley's (Sharpley et al., 1981, 1985; Sharpley and Ahuja, 1982; Sharpley, 1983; Sharpley and Smith, 1989) use of Eq. [3] to predict P in runoff, P_0 was measured by a variety of methods, including extraction by water, NaHCO_3 , and the Bray-1 solution, and isotopic exchange. In our research, Fe-oxide strips were used to measure P_0 . It should be emphasized that the Fe-oxide method is not an absolute measure of desorbable P. Chardon et al. (1996) describe that the Fe-oxide strip method was initially developed for soil chemical studies by Sissinigh (1983) as an alternative to anion exchange resins for estimating the amount of P already sorbed on a soil when determining a P adsorption isotherm. Later, its use was applied to estimate P availability to plants (Menon et al., 1990) and during water quality studies (Sharpley, 1995). The test is appropriate for these uses because the Fe-oxide strip does not react with the soil but rather adsorbs P from the solution, keeps the solution P concentration rela-

tively low, and promotes the desorption of P from the soil to replace the solution P that adsorbed to the strip. Therefore, Fe-oxide strips can be considered to extract that portion of soil P that will easily desorb to water during a relatively short-time period, which in our research was 16 h. We used Fe-oxide strips to estimate P_0 to be consistent with the method used to quantify labile P (desorbable P) in other research conducted in Delaware (Maguire et al., 2000; Pautler and Sims, 2000). Maguire et al. (2000) measured P in 16 Delaware, Maryland, and Virginia Coastal Plain soils with five sequential extractions with Fe-oxide strips. They found that the most P was extracted with the first strip, and the amount of P extracted with the remaining four strips was less than the first strip and was about the same for each strip. As well, Lookman (1995) stated that desorbable P measured with four Fe-oxides strips was consistently greater (as much as four times) than the amount of P that represented a fast desorbing pool in five sandy Dutch soils. Both these research studies suggest that one Fe-oxide strip will extract easily desorbable P, while additional strips will extract consistent amounts of P that represent the P buffering capacity of a soil beyond the fraction of easily desorbable P. Furthermore, Fig. 1c demonstrates that for one of the Sussex County soils used in our research, P_d was well related to P_0 . This trend was true for all our soils. At the widest water/soil ratio (1000:1) and the longest desorption time (180 min), P_d desorbed for all soils was on average 140% of desorbable P measured with Fe-oxide strips. At all other lesser desorption times and water/soil ratios, measured P desorbed was less than desorbable P measured with Fe-oxide strips. This entire discussion above provides evidence that P_0 determined by a single Fe-oxide strip in the Delaware soils represents a reasonable estimate of the amount of P that can be released to water in the desorption times and water/soil ratios used in our research.

An example of the linear relationship between the logarithm of P_d and the logarithm of t for various combinations of W and P_0 is shown for one of the Sussex County soils in Fig. 1a. For all 23 Delaware soils, the values for α ranged from 0.073 to 0.244, with an average of 0.133. Our range and average for α values are very similar to those of Sharpley (1983), which ranged from 0.045 to 0.319, with an average of 0.177. The K values obtained in our study were also similar to those of Sharpley (1983). In the 23 Delaware soils, K ranged from 0.034 to 0.267, with an average of 0.150. In Sharpley's soils, K ranged from 0.021 to 0.302, with an average of 0.142. An example of the linear relationship between P_d and P_0 used to calculate K for various combinations of t and W is shown for the same Sussex County soil in Fig. 1c.

Figure 1b shows the linear relationship between the logarithm of P_d and the logarithm of W for various combinations of t and P_0 for the same Sussex County soil. For all Delaware soils, the values for β ranged from 0.194 to 0.378, with an average of 0.266. These β values were generally less than those of Sharpley (1983), which ranged from 0.204 to 0.850, with an average of 0.520. However, our β values did fall into the lower end of

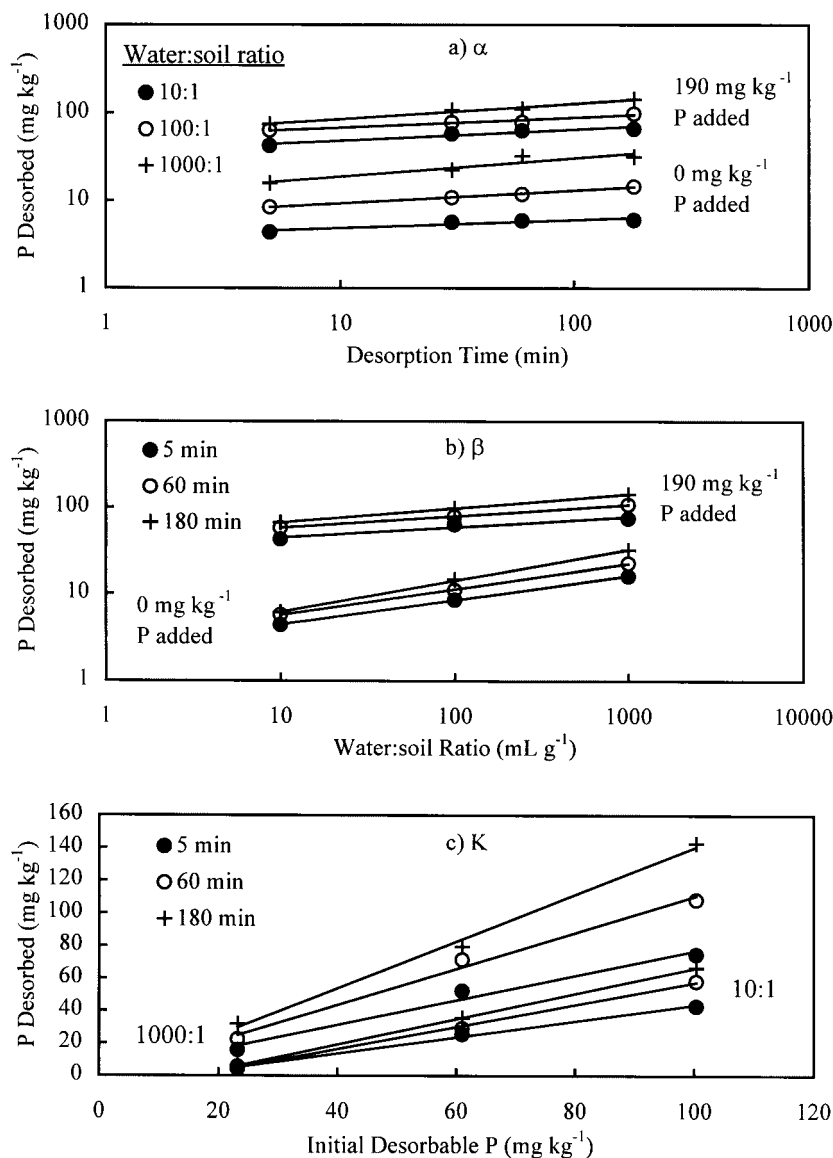


Fig. 1. (a) Relationship between logarithm of amount of P desorbed and logarithm of time or (b) water/soil ratio, and (c) between amount of P desorbed and initial amount of desorbable P for one Sussex County, Delaware soil.

the range of β values measured by Sharpley. This lower end corresponded to his soils that had a low clay/OC ratio. Because the OC values for Sharpley's soils were generally low (range of 7–490 g kg^{-1} , average of 130 g kg^{-1}) and the range in clay content (8–530 g kg^{-1} , average of 220 g kg^{-1}) was broader than that for OC content, his low clay/OC ratios were probably more a result of low clay content than high OC content. Therefore, the range of β values measured in our study, which were similar to those measured for Sharpley's apparently low clay soils, are most likely representative of those that would be obtained for low clay soils. Our 23 Delaware soils can all be considered low clay soils.

Relation of Phosphorus Desorption to Soil Properties

Sharpley (1983) found that K , α , and β were highly correlated with the ratio of extractable Fe/OC and clay/

OC (Table 2). He used these two ratios to represent the *interactive* specific surface area involved in soil P adsorption and desorption. He postulated that adsorption and desorption of P by soils is dominated by sesquioxides or mineral surfaces, and that OC competes with P for adsorption sites, thus decreasing a soil's P adsorption capacity and possibly altering P desorption characteristics. Since soil Fe contents are not usually available from soil survey information, and soil clay content has historically been related with P adsorption parameters, Sharpley used the clay/OC ratio to predict K , α , and β .

The constant α represents a P desorption rate term; and, mathematically, an increase in α results in an increase in the rate of P desorption. Therefore, α should be related to those soil properties that affect how quickly P desorbs from soil. In our study, α values were best correlated, although not significantly, to both $\text{Fe}_{\text{ox}}/\text{OC}$ and clay/OC (Table 2), which is similar to what Sharpley

observed. Therefore, either ratio could be used to predict α values. However, Fe_{ox} was also well related to the K and β values, as discussed below, while clay content was not. So for consistency sake and to minimize the soil analysis required to use Eq. [3], we recommend the $\text{Fe}_{\text{ox}}/\text{OC}$ regression equation (Fig. 2a) to predict α in Delaware and similar Mid-Atlantic Coastal Plain soils.

The ratio of $\text{Fe}_{\text{ox}}/\text{OC}$ was not statistically better correlated to α than the ratio of $\text{Al}_{\text{ox}}/\text{OC}$, although its r value was numerically greater. However, desorption of P from Fe hydroxides may be more affected by desorption time than desorption of P from Al hydroxides. Lookman (1995) investigated P desorption from synthetic amorphous coprecipitates of Fe and Al with phosphate. He found that in desorption experiments of times up to 1004 h, the rate of P desorption from Fe hydroxides consistently decreased with desorption time, but the rate of P desorption from Al hydroxides was more or less constant for all times of desorption. Also, more P was desorbed from Fe hydroxides than from Al hydroxides in the first 400 h. This trend was reversed at desorption times >400 h. Lookman speculated that P associated with the Fe was present as a surface adsorbate and not a precipitate, thus providing more P in contact with the solution that could desorb quickly and less P that would slowly diffuse from interior sites of precipitates. Com-

paratively, P desorption from Al hydroxides may have been a process of continuous slow dissolution of the Al phosphate phase. Lookman's research provides evidence for why the α value for P desorption in Delaware soils was better correlated to the ratio of $\text{Fe}_{\text{ox}}/\text{OC}$ than $\text{Al}_{\text{ox}}/\text{OC}$.

Including the OC parameter in the regression equations generally improved the ability to predict α , although not always significantly. This suggests that the association of OC with Fe or Al hydroxides in soil can increase the rate at which P is desorbed from soil. This could be because of the ability of OC to maintain Fe and Al hydroxides in poorly crystalline forms that are more susceptible to P desorption (Toor and Bahl, 1999), the replacement of P on soil surfaces with organic anions, or the formation of soluble complexes between Al and organic anions that can prevent reprecipitation of desorbed P (Fox et al., 1990; Bhatti et al., 1998).

During a P desorption event, if the water/soil ratio increases, for example because of an increase in soil water content or in the amount of runoff, P will desorb from the soil to maintain an equilibrium between the soil and solution. A soil that has a relatively large capacity to supply P to the soil solution can be considered well buffered against changes in solution P concentrations. This soil may therefore exhibit fairly uniform P desorption under various water/soil ratios. Phosphorus desorption in a poorly buffered soil is more influenced by changing water/soil ratios. The value of β for a given soil reflects this buffering phenomenon because it is the exponent for the variable W in Eq. [3]. As β increases, dilution of the interacting soil and water has a greater influence on P desorption. Therefore, β should be related to those soil properties that determine a soil's P buffering capacity. Unlike Sharpley (1983), we found that β values in our Delaware soils were not well correlated to the ratios of $\text{Fe}_{\text{ox}}/\text{OC}$ or clay/OC (Table 2). The best relationship observed between β and soil properties was with the sum of Fe_{ox} and Al_{ox} , although not statistically better than the relationship with Al_{ox} or Fe_{ox} alone. In our primarily sandy, low clay Delaware soils, Fe and Al hydroxides dominate P sorption and therefore represent the interactive soil surfaces from which P will desorb (Pautler and Sims, 2000). An increase in $[\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}]$ represents an increase in P buffering capacity, and thus an increase in β . This is consistent with the data in Fig. 2b, which shows how β increases with increasing content of $[\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}]$. Including OC in the regression equations generally did not improve, and sometimes significantly decreased, the ability to predict β . This suggests that while OC may affect the rate at which P desorbs from these Delaware soils, as seen with the α data, it may not affect their overall P buffering capacity.

As with the β results, K values seemed to be best related to soil $[\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}]$, although not statistically better than with Al_{ox} alone or the ratios of $\text{Fe}_{\text{ox}}/\text{OC}$ or clay/OC (Table 2). The constant K represents a P desorbability or capacity term. It expresses the proportion of available soil P that can be desorbed from a soil for a given time and water/soil ratio. An increase in K means that the proportion of P_0 desorbed from a soil

Table 2. Relationships between the constants of Eq. [3] and selected soil properties for 43 national soils (Sharpley, 1983) and 23 Delaware soils.

Regression Equations				
Sharpley's 43 soils				
α	=	$0.314 (\text{Extr. Fe/OC})^{-0.327}$	$r = 0.74^{***}$	
β	=	$0.291 (\text{Extr. Fe/OC})^{0.268}$	$r = 0.79^{***}$	
K	=	$0.325 (\text{Extr. Fe/OC})^{-0.496}$	$r = 0.81^{***}$	
α	=	$0.779 (\text{Clay/OC})^{-0.526}$	$r = 0.83^{***}$	
β	=	$0.143 (\text{Clay/OC})^{0.419}$	$r = 0.82^{***}$	
K	=	$1.327 (\text{Clay/OC})^{-0.806}$	$r = 0.81^{***}$	
Delaware's 23 soils				
α	=	$0.215 (\text{Clay/OC})^{-0.270}$	$r = 0.84^{ab***\dagger}$	
α	=	$0.024 (\text{Fe}_{\text{ox}}/\text{OC})^{-0.346}$	$r = 0.86^{a***}$	
α	=	$0.022 (\text{Al}_{\text{ox}}/\text{OC})^{-0.495}$	$r = 0.62^{abcd**}$	
α	=	$0.019 ((\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})/\text{OC})^{-0.577}$	$r = 0.78^{abc***}$	
α	=	$0.233 (\text{Clay})^{-0.294}$	$r = 0.43^{cd*}$	
α	=	$0.157 (\text{Fe}_{\text{ox}})^{-0.102}$	$r = 0.13^d$	
α	=	$0.050 (\text{Al}_{\text{ox}})^{0.286}$	$r = 0.58^{abcd**}$	
α	=	$0.044 (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{0.296}$	$r = 0.53^{bcd*}$	
β	=	$0.270 (\text{Clay/OC})^{-0.019}$	$r = 0.16^{bc}$	
β	=	$0.217 (\text{Fe}_{\text{ox}}/\text{OC})^{-0.039}$	$r = 0.16^{bc}$	
β	=	$0.389 (\text{Al}_{\text{ox}}/\text{OC})^{0.111}$	$r = 0.23^{bc}$	
β	=	$0.325 ((\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})/\text{OC})^{0.060}$	$r = 0.14^c$	
β	=	$0.244 (\text{Clay})^{0.076}$	$r = 0.18^{bc}$	
β	=	$0.158 (\text{Fe}_{\text{ox}})^{0.247}$	$r = 0.52^{abc*}$	
β	=	$0.134 (\text{Al}_{\text{ox}})^{0.203}$	$r = 0.67^{ab**}$	
β	=	$0.107 (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{0.251}$	$r = 0.72^{a***}$	
K	=	$0.078 (\text{Clay/OC})^{0.286}$	$r = 0.55^{ab**}$	
K	=	$0.858 (\text{Fe}_{\text{ox}}/\text{OC})^{0.382}$	$r = 0.59^{ab**}$	
K	=	$0.255 (\text{Al}_{\text{ox}}/\text{OC})^{0.174}$	$r = 0.14^b$	
K	=	$0.428 ((\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})/\text{OC})^{0.347}$	$r = 0.29^b$	
K	=	$0.183 (\text{Clay})^{-0.138}$	$r = 0.13^b$	
K	=	$0.311 (\text{Fe}_{\text{ox}})^{-0.399}$	$r = 0.32^b$	
K	=	$1.239 (\text{Al}_{\text{ox}})^{-0.669}$	$r = 0.84^{a***}$	
K	=	$2.168 (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{-0.773}$	$r = 0.85^{a***}$	

* Significant at the 5.0 probability level.

** Significant at the 1.0 probability level.

*** Significant at the 0.1 probability level.

† For the 23 Delaware soils, correlation coefficients with different letters are significantly different at the 5% probability level, as compared only within the group of equations for K , α , or β .

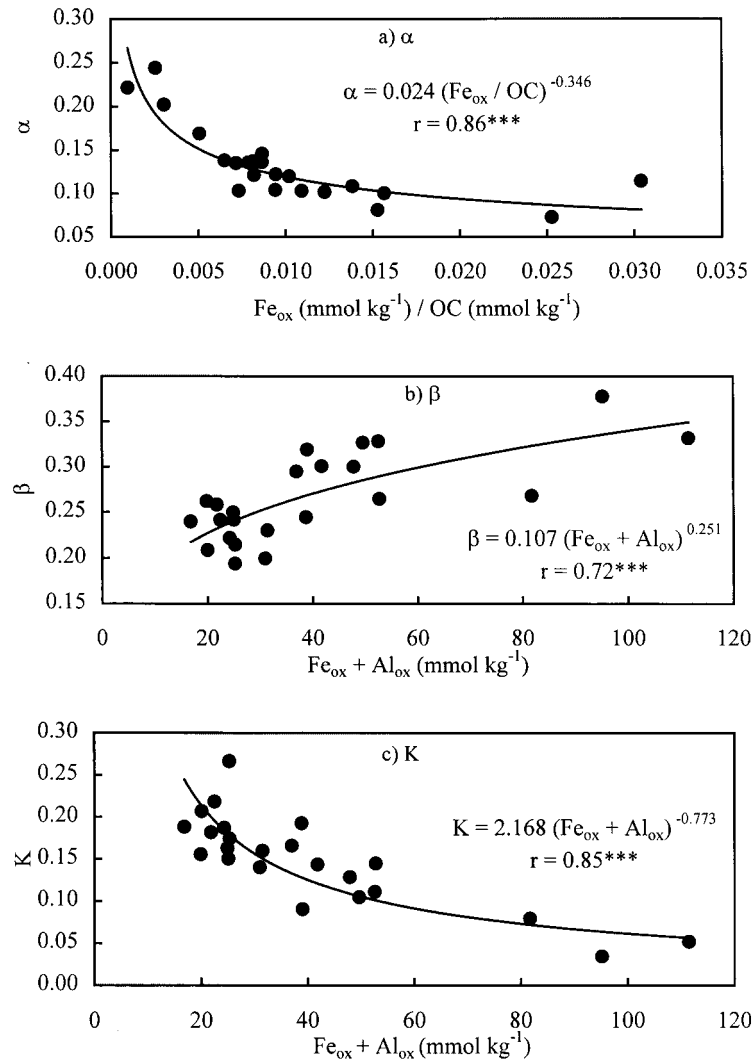


Fig. 2. Relationship between soil properties and the constants (a) α , (b) β , and (c) K for 23 Delaware soils.

will also increase. This may be attributed to low soil sorption capacity, which in Delaware soils is represented by a low content of $[\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}]$. This is consistent with data in Fig. 2c, which shows that as $[\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}]$ increases, the P sorption capacity of the soil increases, and the K value subsequently decreases. As with the β results, including OC in the regression equations changed the exponent from negative to positive and significantly decreased the ability to predict K when Al was included as a factor. When Fe or clay was included as a factor, including the OC parameter in the regression equations also changed the exponent from negative to positive, but did not statistically change the ability to predict K , although the r values for the equations including OC were numerically greater. This difference in the effect of OC on Al and Fe and clay may be because Al is more typically complexed with soil OM than Fe or clay.

In summary, the following equations are proposed for predicting α , β , and K values for Delaware and similar Mid-Atlantic Coastal Plain soils:

$$\alpha = 0.024 (\text{Fe}_{\text{ox}}/\text{OC})^{-0.346} \quad [4]$$

$$\beta = 0.107 (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{0.251} \quad [5]$$

$$K = 2.168 (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{-0.773} \quad [6]$$

The relationships between soil properties and the values of α , β , and K as described by Eq. [4] through [6] were all statistically significant at the 0.1% probability level; and all coefficients in Eq. [4] through [6] were statistically significant at the 5.0% probability level. Also, even though Eq. [4] through [6] were determined using data from only Delaware soils, they should be applicable to similar soil types in the Mid-Atlantic Coastal Plain. It is important to emphasize that those relationships developed by Sharpley (1983) to predict α , β , and K should still be used for soils that are chemically and physically similar to the ones he used. For soils that are similar to our 23 Delaware soils, Eq. [4] through [6] may provide a better prediction of α , β , and K and thus of P desorption.

Predicting Phosphorus Desorption

To determine if the relationships to predict K , α , and β as proposed by Sharpley (Table 2) were accurate for Delaware soils, Eq. [3] was tested for its ability to predict

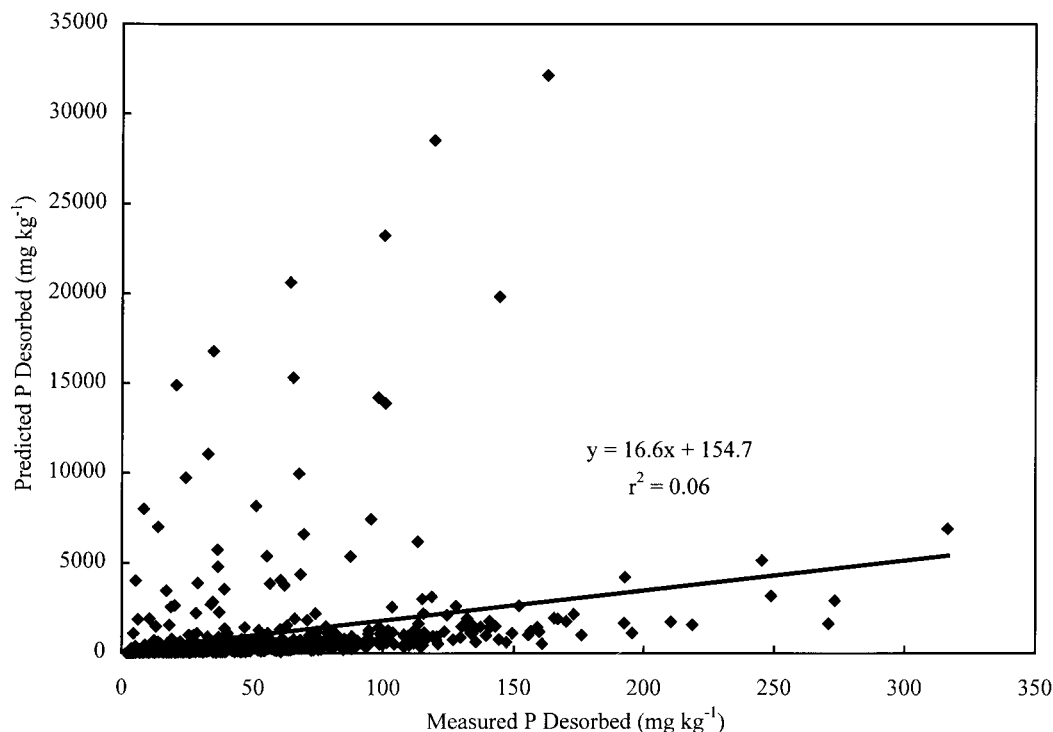


Fig. 3. Relationship between P desorbed estimated using Eq. [3] and values of α , β , and K calculated from equations of Sharpley (1983) for clay/OC as presented in Table 2 and P desorbed as measured under the same experimental conditions of time, water/soil ratio, and P_0 content for 23 Delaware soils.

P desorption. First, K , α , and β were calculated for the 23 Delaware soils using Sharpley's recommended clay/OC equations. Values for t and W in Eq. [3] were taken from the specific methods of our desorption experiments, and values for P_0 in Eq. [3] were taken from the quantities of desorbable P as measured in all soils before the desorption experiments. Then, Eq. [3] was used to predict P desorption for all soils and all combinations of t , W , and P_0 . The predicted amounts of P desorbed were then compared with the amounts of P desorbed as measured during the desorption experiments. Figure 3 shows that using Sharpley's equations for Delaware soils resulted in a very weak relationship between measured and predicted P desorption. These results suggest that the equations recommended by Sharpley to predict values for K , α , and β may not provide a good prediction of P desorption for our Delaware or similar Mid-Atlantic Coastal Plain soils. Therefore, Eq. [4] through [6] will likely provide a better prediction of P desorption for Delaware and Mid-Atlantic Coastal Plain soils. These equations are currently being tested using several independent data sets collected during simulated rainfall experiments using Delaware soils to better assess their potential to predict P desorption and to justify their incorporation into the FHANTM 2.0 model for use in Delaware and the Mid-Atlantic Coastal Plain.

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